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14. ABSTRACT

Thin barium strontium titanate (BST) films are being developed as dielectric film for use in tunable radio frequency (RF)/microwave applications. Thin BST film capacitor devices were fabricated using physical and chemical solution deposition techniques. The typical dielectric constant of the physical deposition via RF magnetron sputtering film capacitors was in the range of 480–780 and had dissipation factors between 0.01 to 0.06 with conventional annealing. After the effect of postamalgamate processing technique via photon ultraviolet (UV) irradiation annealing, these losses showed further improvement. In addition, BST films processed via solution metal organic spin deposition, which yield a lower dielectric range of 150–335, also showed improved loss with UV processing from 0.014 to 0.010 while effectively maintaining desirable electrical properties. The dielectric properties of these films had little dependence on frequencies from 100 KHz to 1 MHz. The physical properties revealed that the thin films are crystalline with no evidence of any secondary phases.

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1. Introduction

Thin film barium strontium titanate (BST) is a promising complex oxide material for active elements in tunable devices such as filters, varactors, delay lines, phase shifters, DC-DC converters, and voltage controlled oscillators.[1–7] To achieve any useable properties, the materials must be microwave friendly, particularly the properties of dielectric, loss, and tunability. In the last decade, there have been several efforts aimed at lowering thin film BST dielectric loss, including acceptor doping, processing method, modification of configuration, improving film/electrode layer interface, and adhesion via buffer layers. This report details how we used solution and physical deposition to fabricate thin films via radio frequency (RF) sputtering and metal organic spin deposition (MOSD). BST (60/40) thin films (~200 nm thickness) were RF sputtered from a circular solid stoichiometric ceramic target onto platinum silicide (PtSi) and r-plane sapphire substrate, and MOSD films were deposited using a precursor described in previous reports.[6] The as-deposited films were annealed via straight substrate conventional thermal annealing and ultraviolet (UV)-assisted photon irradiation annealing at various temperature. We will discuss the BST thin films process and effect of postamalgamate processing technique, which combines MOSD and RF sputtering with photons in the UV range irradiation annealing to achieve balanced and desirable BST material properties.

2. Experiment

The fabrication of thin and thick films has been reported using many techniques, such as sol-gel, hydrothermal, electrophoretic, reactive partially ionized beam deposition, and metal organic chemical vapor deposition. Each of these techniques offers many advantages and disadvantages, and some may require high cost investment, complicated apparatus, and complex sets of deposition parameters. For this report, BST thin films were deposited by 2 different methods: metal organic solution deposition and RF magnetron sputtering. RF sputtering deposition relies on a “fourth state of matter”, a plasma that is created by an ionized argon/oxygen gas mixture. This mixture consists of positively charged ions and negatively charged electrons ignited using an oxygen-assisted strike. In a controlled atmospheric condition and temperature, the materials will bombard from a 4-inch circular BST sintered ceramic target a few atoms at a time. RF sputtering is one of the most versatile deposition techniques, particularly in multicomponent or mixtures form because it can be processed from one formulated target as compared to chemical vapor deposition, where each component requires a different precursor

and is likely to evaporate and control at different temperature and rates. Similar to MOSD, RF sputtering is also compatible with the industry foundry process, but the one drawback is that sputtering's coverage is less conformal. For now, it is more widely used in the 2-dimensional application such as memory optical technology.

We used a Lesker PMS-18 vacuum system prepared with a ceramic target approximately 40° off x-axis to deposit onto a silicon (Si) wafer. A load lock and a residual gas analyzer were used as part of reduction and monitor contamination. Cleaning steps included argon surface cleaning followed by a thin layer of titanium (Ti) as a support adhesion layer.[7] Finally, an estimated 150- to 200-nm-thick layer of BST was deposited. Including off axis angle, gas mixture ratio, pressure, and throw distance, deposition took around 4–6 h to yield desirable thickness. A substrate holder with a heater and rotation capability was used to in situ anneal the film. The target temperature during sputtering ramped up to 700 °C. RF power has a ramp rate both up and down cooling of approximately 0.33 W/min to prevent thermal shock, which might damage the target; deposition rate was about 0.83 nm/min. All films were deposited at a base pressure below 6.0×10^{-8} Torr, while the argon/oxygen pressure ratio at 90:10 during sputtering was maintained at 2×10^{-3} Torr. For MOSD films, BST spin coating was deposited onto a plane of PtSi substrate at various velocities to centrifugally spread the solution over the substrate. Thicknesses can be controlled by the speed at which the solution is spun, and the viscosity plus the number of layers of the solution determines the ultimate thickness of the deposited film. The advantage of MOSD processing includes low processing temperature, precise composition control, low equipment cost, and uniform deposition over large area substrates.[6,7] To fabricate these thin films, barium acetate, strontium acetate, and titanium isopropoxide were selected as precursors, and 2-methoxyethanol was chosen as a solvent. Barium acetate and strontium acetate were initially dissolved in glacial acetic acid. The clear solutions, thus formed, were added to the solution of titanium isopropoxide in 2-methoxyethanol to control viscosity and to prepare a stoichiometric, clear, and stable BST precursor solution. The details of processing MOSD were described in previous publications.[3–7]

Glancing angle X-ray diffraction, using a Bruker D5005 diffractometer with CuKa radiation, was employed to assess film crystallinity. A Digital Instruments Dimension 3100 atomic force microscope (AFM) and a Hitachi S4700 field emission scanning electron microscope (SEM) were used to assess film surface morphology. The UV photon annealing set of films were in situ annealed at 700 °C and times of 0, 120, and 225 min in a custom built load lock annealing chamber modified from a pulsed laser chamber system (Fig. 1). The annealing chamber was designed with a substrate heater, precision oxygen, partial oxygen pressure control

at 100 mTorr, and equipped with in situ photon UV grid lamp sources facing the sample for performing UV-assisted annealing. The UV photon source was approximately 7 cm from the sample and produced radiation between 185 and 254 nm and is operated at 50 mW/cm^2. A bottom electrode and a circular platinum shadow mask to create a metal/insulator/metal (MIM) configuration was used for the dielectric properties of the film. A reactive ion etcher was then used to expose the bottom electrode. It was measured in terms of the dielectric constant (ε_r) and dissipation factor (tan δ). The capacitance measurements were conducted using a HP impedance gain phase analyzer 4194A by applying a small AC signal of 10-mV amplitude and 100-KHz frequency across the sample.

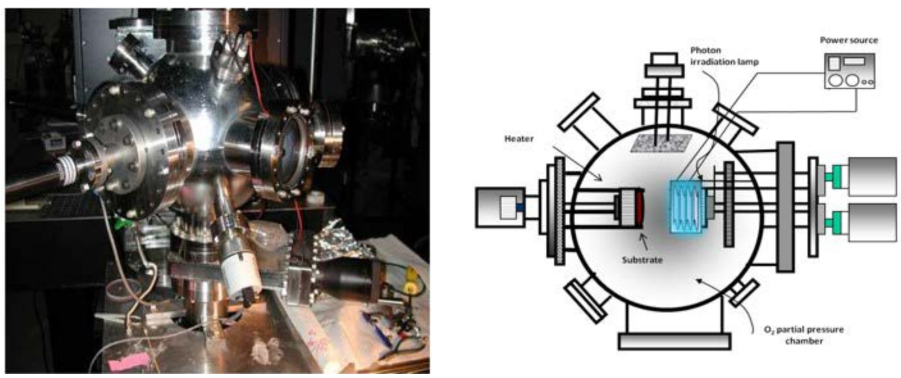


Fig. 1 Modified in situ photon UV annealing chamber

3. Results

For many years, researchers made numerous attempts to improve the thin film of BST for various applications. The objectives were to enhance dielectric loss, dielectric tunability, and ε_r response at a higher frequency. The various efforts included formula alteration, method of processing, physical modification, improving film/electrode layer interface, and adhesion via buffer layers.[8–13] Some results achieved a certain aspect of the electrical properties; however, often at the expenses of processing capital cost and most important, of the other useful properties. Consequently, an emphasis on developing new materials, incorporated with conventional industry processing methods, will progress toward achieving useful electrical properties tunability loss while remaining focused on affordability. We will discuss some of the findings in our research.

3.1 Physical Properties

The X-ray diffraction (XRD) (Fig. 2) studies were performed on both MOSDs and sputtered with conventional annealing thin films. Both results show that the X-ray patterns has no evidence of secondary phase formation, as no peaks other than 100,

110, 111, 200, 211, and BST peaks were observed. XRD was used to assess the crystallinity, lattice parameters, and the grain size of the thin-film materials. A Rigaku diffractometer with 40-kV CuKa radiation was used. The glancing angle was optimized for each specimen between 1° and 4°. The crystalline phase of the thin films was identified by comparing the X-ray diffraction peaks of the thin films with those of previously reported films.[8,9] In sputtered film, a thin 30-nm Ti layer seems to facilitate the adhesion and integrity of the films to the substrate. MOSD and sputtered film (Fig. 3) show no signs of cracking or peeling; the surface morphology of the modified BST thin films was observed by AFM.

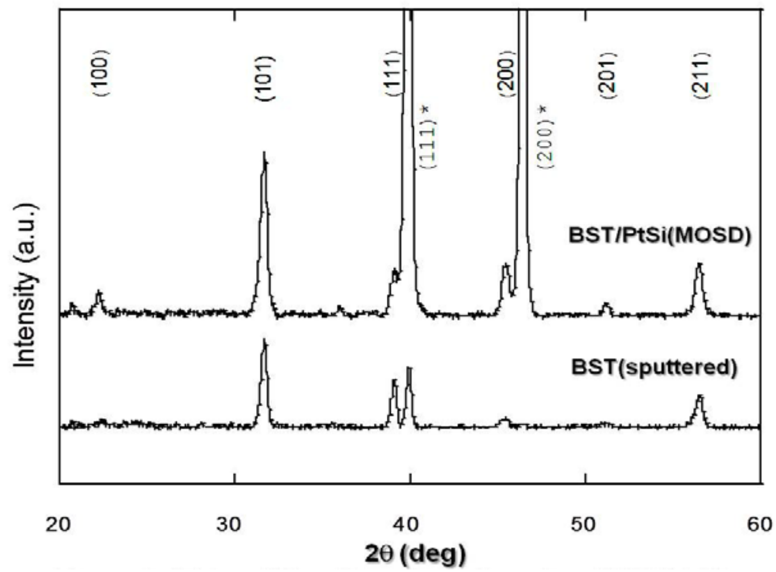


Fig. 2 X-ray diffraction of sputtered and MOSD films

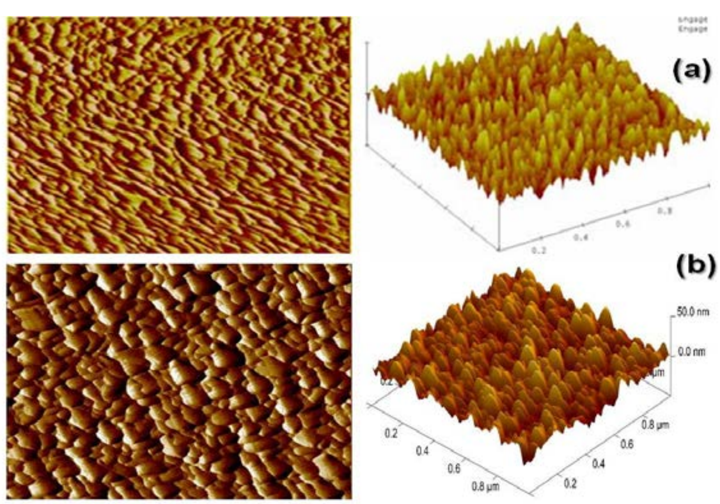


Fig. 3 AFM of $BaSrTiO_3$; the scale bar indicates height. Surface roughness of a) MOSD is 2.226 nm and b) RF magnetron sputtered thin film is 2.3 and 5.04 nm with randomly distributed grains. Scanned area is 1 × 1 µm.

Figure 3 shows the comparison of a micrograph of the 1 × 1 μm scan area of a BST sample. Surface roughness was around 5.07 and 2.30 nm for sputtered as compared to MOSD, although both films exhibited a dense microstructure with a very fine grain size. Physical deposition, such as pulsed laser and sputtering, has more bombarded pronounce growth, which typically yields a columnar crystalline habit. Thus, physical deposition has higher surface roughness than solution deposition as seen in similar published results[8,9] and as indicated by the average surface roughness values. Surface roughness, pin-holes, and hillocks in the electrode can lead to additional scattering and attenuation. Hence in sputtering films dielectric properties have a potential in reflecting higher loss. However, the SEM and cross section (Fig. 4) revealed that before and after annealing a typical microstructure of these films was continuous, dense, smooth, and uniform in grain size.

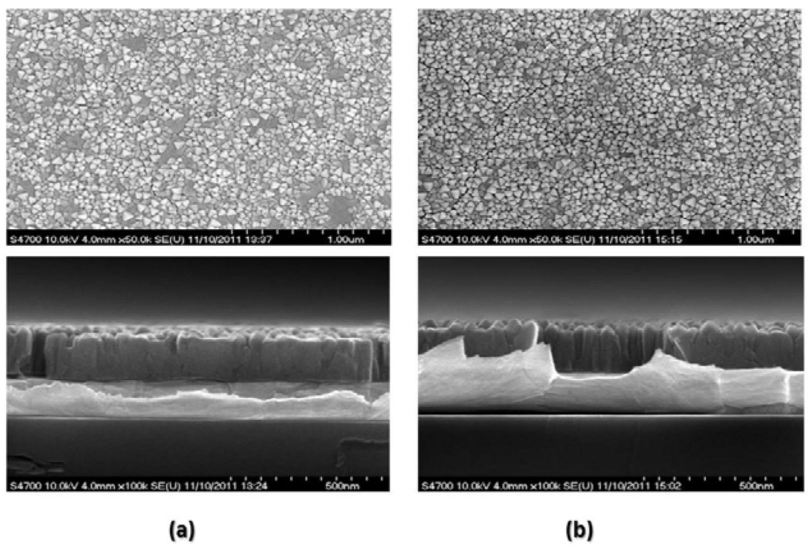


Fig. 4 Typical RF sputtered BST thin film: at a) no UV and b) at 225 min UV annealed

3.2 Dielectric and Insulating Properties

To further examine the quality of the BST thin films, the ferroelectric properties of the films were measured in a MIM configuration. All BST films were uniformly deposited on 50.8-mm wafers, thus signifying reproducibility and uniformity throughout the wafer and most important, the suitability for industry foundry production. The dielectric properties were measured for the ε_r and dissipation factor. The BST capacitors are modeled in terms of an impedance equivalent model circuit. The series resistor represents electrode loss, and the parallel resistor-capacitor circuit represents the capacitance and the dielectric loss, assuming lead inductance is negligible. The HP 4294A impedance analyzer meter can measure the capacitance as a function on frequency in parallel model known as C_p or in series known as C_s (Fig. 5a and 5b). The chosen circuit model was dependent on the value

of overall capacitance of the capacitor. Since our films have relative low capacitance and are high in impedance, parallel impedance between the film capacitor and the parallel resistor will become significantly higher than the series resistor. Therefore, applying general electrical engineering standard measurement technique, we set the model circuit for measuring capacitance to C_p model. In addition, significant steps were made to ensure accuracy of measurement including parasitic, admittance, and reference point compensation by reducing cable length. We also enhanced electrode contact with silver paint and melted indium probing, particularly for grounding side. The final step is a calibration of a full spectrum using Picoprobe GGB Industries pad Model CS-8 via short, open, and load to reduce and overall eliminate stray capacitance. To add adhesion and bottom electrodes, a stack layer of Ti and Pt was deposited, respectively. It was reported that such bilayers show good electrical conductivity, high temperature stability, excellent diffusion barriers up to high processing temperatures of 700 °C, and good adhesion with the ferroelectric thin film and Si substrate.[8] This ε_r value for both types of films was reasonable as compared to the typically reported value of 60.40 for pure BST thin films. The measured typical ε_r of these film capacitors was in the range of 480–780 for sputtered and 150–335 for processed via MOSD. Figures 6a and 6b shows the small signal ε_r and dissipation factor as a function of frequency. For dielectric properties that show a slight dispersion decrease in the frequency spectrum, a sweep up to 100 MHz indicates the absence of any surface layer or electrode barrier effects in capacitance measurements. These film capacitors had dissipation factors between 0.01 and 0.16 with conventional annealing. The loss, however, shows characteristics of improvement via UV annealing at 120 min from 0.014 to 0.009, which potentially indicate the advantage of postamalgamate processing of irradiation annealing. The changes in this loss will require additional research to confirm search findings, including leakage current. Leakage is a tremendous factor to retain stored energy and usefulness for a tunable applications, particularly to minimize energy power consumption.

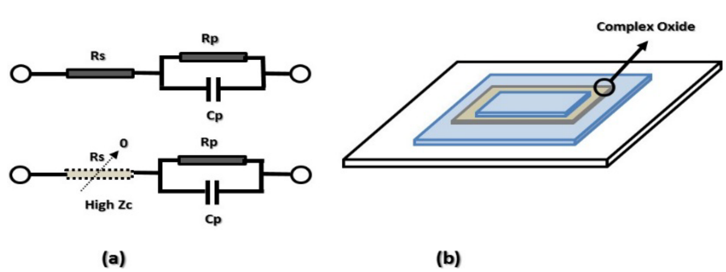
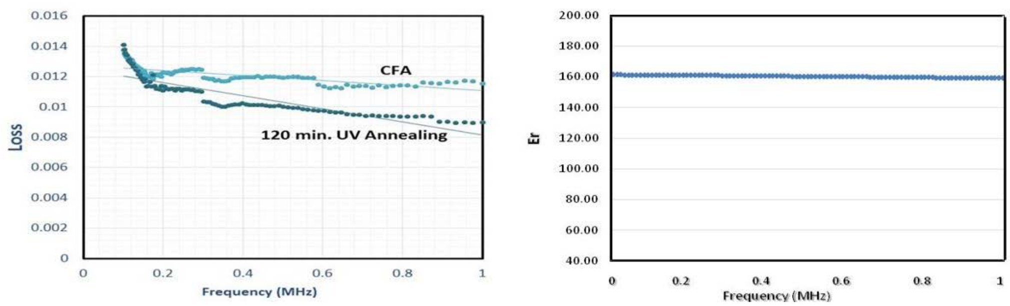


Fig. 5 a) Impedance equivalent circuit and b) complex oxide thin film on substrate



(a) (b)

Fig. 6 a) Loss vs. frequency for conventional furnace annealing and 120 min UV annealing of MOSD film and b) ε_r vs. frequency sweep

4. Conclusion

Thin BST film capacitor devices were fabricated using physical and chemical solution deposition techniques. The XRD studies were performed on MOSD and sputtered film with conventional annealing thin films. MOSD and sputtered film showed no signs of cracking or peeling; the surface morphology of the modified BST thin films was observed by AFM. The physical deposition of the BST sample had a surface roughness around 5.07 nm as compared with solution deposition of 2.30 nm. Both films exhibited a dense microstructure with a very fine grain size. However, the loss shows a characteristic of improvement via UV annealing at 120 min from 0.014 to 0.009, which potentially indicates the advantage of postamalgamate processing of irradiation annealing. Future studies and characterization are required to confirm search findings, including leakage current. The experimental work suggests that UV annealing processed possibly resulted in improvement in dielectric loss, which is crucial to the realization and commercialization of low-cost tunable application.

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List of Symbols, Abbreviations, and Acronyms

AFM	atomic force microscope
BST	barium strontium titanate
ε_r	dielectric constant
MIM	metal/insulator/metal
MOSD	metal organic spin deposition
PtSi	platinum silicide
RF	radio frequency
SEM	scanning electron microscope
Si	silicon
Ti	titanium
UV	ultraviolet
XRD	X-ray diffractometry

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